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ON THE SPECTROSCOPIC EXAMINATION OF POSITIVE RAYS ISOLATED BY TRANS-MISSION THROUGH THIN PARTITIONS.

BY

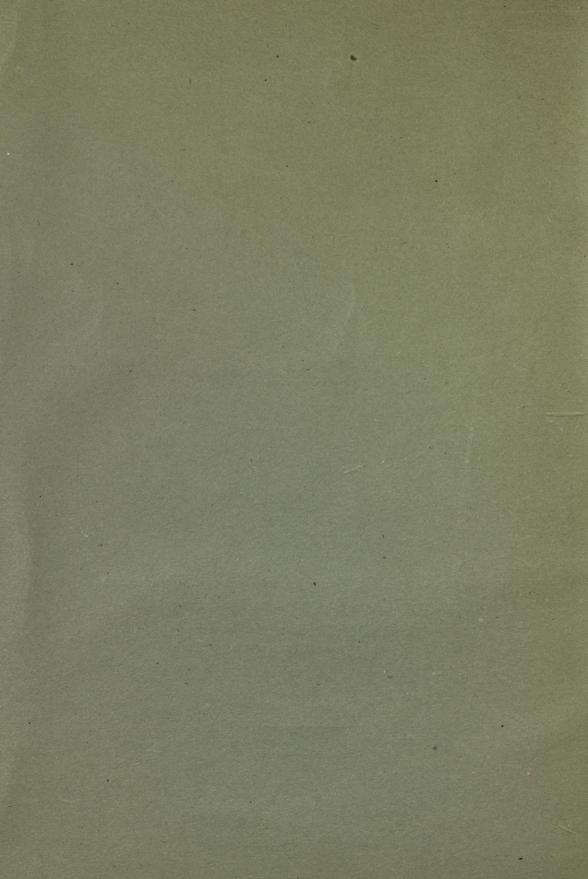
ALFRED NORTON GOLDSMITH.

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN

THE FACULTY OF PURE SCIENCE,

COLUMBIA UNIVERSITY.



ON THE SPECTROSCOPIC EXAMINATION OF POSITIVE RAYS ISOLATED BY TRANSMISSION THROUGH THIN PARTITIONS.

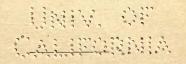
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ON THE SPECTROSCOPIC EXAMINATION OF POSITIVE RAYS ISOLATED BY TRANSMISSION THROUGH THIN PARTITIONS.

BY ALFRED N. GOLDSMITH.

I. INTRODUCTION.

THE canal rays were discovered by Goldstein in 1886, and through the researches of W. Wien in 1898, and later of Sir J. J. Thomson, their identity with the positive ions was definitely established. They have been frequently employed since as a source of positive ions for investigation of the properties of positive electricity.

The mode of production of the canal rays involves the use of a perforated cathode in a tube containing a gas at low pressure through which an electric discharge is passing. Back of the perforation in the cathode will be found a column of rapidly moving positive ions, their presence being detectable by the fluorescent, photographic and electrostatic effects which they can produce. J. Stark¹ discovered the Doppler effect which is displayed by the canal rays behind the cathode, as evidenced by the shift of the lines of the spectrum when viewed respectively in directions perpendicular and parallel to the direction of motion of the ions. His experiments showed that the velocity of the positive ions was the same as the velocity of the ions when measured by means of the "magnetic and electric spectra." The magnetic and electric spectra are obtained when the ions pass through strong electric and magnetic fields. From the observation of the resulting deflections of the beam of canal rays it is possible to evaluate e/m and v.

In 1907 Thomson² showed, by examination of the magnetic spectrum obtained in gases which had been as carefully as possible freed from all traces of hydrogen that the value of e/m for some of the positive ions was (10)⁴, 5(10)³, and 2.5(10)³. The two former values correspond to the hydrogen atom and molecule, and the latter to the helium atom. At lower pressures in all gases, positively charged atoms of hydrogen were found to be present in spite of the attempts at purification of the gas. W. Wien then

called attention to his earlier hypotheses that the positive ions lose their positive charge, that is, are neutralised at some point of their path and then may be again positively electrified by the loss of negative electrons, and also that ions of larger mass than those usually found exist in the discharge. His conclusion³ that the hydrogen found in the discharge tube was present only as an impurity was disputed by J. J. Thomson⁴, who found that even when the amount of hydrogen was greatly changed, its presence did not become more prominent. He suggested later⁵ that, reasoning from the constancy of the velocity of the canal and retrograde rays, they owe their velocity either to an explosion in the atom or their charge is different at different points of their path. Possibly both causes are operative. Wien's hypothesis of the existence of neutralised positive ions in the canal rays was shown to be well-founded by experiments undertaken by Thomson in 1908.^{6 & 7}

W. Wien found⁸, reasoning from the experimentally determined magnetic deflections of the positive ions in the canal rays, that the greatest velocity they attained was that which would be given to a positively charged atom of the gas which owed its velocity to the potential gradient actually existing in the tube.

As early as 1903, J. Stark⁹ had suggested that neutral doublets or even negatively charged canal rays might be produced, and that these, moving with high velocities, would cause effects similar to those produced by the positive ions.

O. Reichenheim¹⁰ showed that in the canal rays in oxygen there are three kinds of ions prominently present, namely the hydrogen atom, the hydrogen molecule, and the oxygen atom. In general the spot of light in the magnetic spectrum corresponding to the hydrogen atom is the most evident. Similarly, the presence of the hydrogen atom in the cases where the tube was filled with argon or nitrogen was observed, though in these cases it was not easy to find the charged atoms of the gas filling the tube.

A recent research of Thomson¹¹ established the existence of three kinds of canal rays. Firstly, rays which are not deflected by electric or magnetic forces. Secondly, "secondary rays" which are produced by the collision of rays of the first kind with the molecules of the gas. Thirdly, rays which appear at low pressures, have velocities proportional to the difference of potential between the electrodes, and for which e/m is inversely proportional to the atomic weight of the gas in the tube. The secondary rays always

have a velocity of 2(10)⁸ cm. per second and a value of e/m of 10⁴. That their velocity is independent of the potential difference between the electrodes suggests that they may be produced by the dissociation of the molecules of the gas by a sort of trigger action, and their energy comes from the store of molecular energy originally present.

Certain properties of the α rays from radium are of interest and will be briefly considered. Bragg and Kleeman¹² first discussed the diminution of velocity of the α particles which was sufficient to cause them to lose their ionising power. They found that the critical velocity was about 1.5(10)⁹ cm. per second, which is 60% of the initial velocity of the homogeneous rays from Radium C. It is quite possible that uncharged particles not electrically detectable can continue passing through matter even at the end of their so-called range, for it is a very improbable assumption that the velocity suddenly falls from the critical value to zero.

The most important work as to the actual nature of the α rays was done by Rutherford and Royds. By passing the α particles through the walls of a thin glass chamber (0.01 mm. thick) into a space exhausted to a high vacuum and compressing the trapped gas in a tube where its spectrum could be examined, they succeeded in definitely proving that the α particle after losing its positive charge was helium. The spectrum of the helium gradually developed in the spectrum tube, in some cases taking as long as six days to become completely visible. Check experiments were performed to test for possible diffusion or leakage of the gas through the thin glass containing tube. The method of isolation of positive rays by transmission through thin partitions, so successfully employed by Rutherford in this instance, was used in the present research into the nature of the canal rays.

II. OBJECT OF THE RESEARCH.

The following experiments are an attempt to pass the canal rays through a thin diaphragm into a highly vacuous separate chamber where the spectrum of the accumulated gas, if any, can be examined free from disturbances of the electric discharge which produced the canal rays.

III. DESCRIPTION OF THE APPARATUS.

The discharge tube used in the experiments is shown in figure 1. The anode is A; and B, a ring of aluminum with a large hole in its center is the cathode. The potentials used were at times so high that it was difficult to secure high insulation because of surface leakage over the glass. Therefore the terminal wires were run from the platinum leading-in wires at S and P to the points T and Q through glass tubes which were sealed in place and of which the ends were filled with sealing wax. Connection to the pumps was secured by a side tube at F. To prevent the canal rays striking the edge of the disc U (where the sealing cement was occasionally present) a guard ring was placed at L.

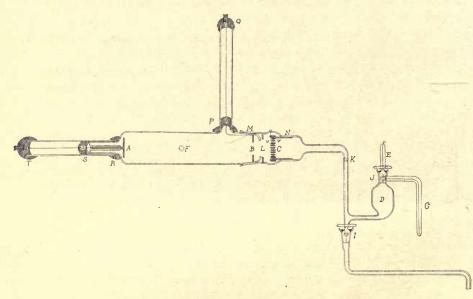


FIGURE 1.

It was desirable at times to remove the plug C and the diaphragm carried therein without rebuilding the portion of the apparatus surrounding it, and this became possible by placing a ground joint at M. The thin partition used in the experiments was carried on the front face of the steel plug C, this face being perforated with circular holes I mm. in diameter. The thin diaphragm, through which the canal rays passed, was sealed with

cement on the front face of C. The cement was very carefully placed so that none of it was in the path of the moving ions. Over the diaphragm was fastened the plate U, which had in it holes coinciding in size and position with those in V. The plate U was screwed to V at the edges after cement had been placed on the back of U to fasten it gas-tight to the diaphragm. As before, the cement was carefully kept out of the path of the ions. The steel plug fits into place at N. In order to connect that portion of the apparatus which is back of the diaphragm to the vacuum pumps an outlet with a stop-cock was placed at K. Connection with a mercury reservoir was secured through the tube H; I is a mercury-sealed stop-cock to the small discharge tube E, which is of fairly fine capillary tubing. Connected to E is G, a piece of the finest capillary tubing.

It will be seen that the vacuum apparatus is really two chambers, AB and CD, which are divided by the air-tight partition at U. This partition was thin enough to permit the penetration and passage of the positive rays. These particles at high velocities were thus passed from the chamber AB to the chamber CD, where they accumulated and were examined.

Experiments were tried in air, carbon dioxid, hydrogen, argon, and helium. The argon was prepared by sparking air in the presence of an excess of oxygen, which excess of oxygen was afterward removed by yellow phosphorus. Helium was produced with the same apparatus except that instead of starting with air, the gas obtained by heating monazite sand was used. Since this gas is a mixture of air and helium, it was not difficult to secure rapidly the necessary amount of helium.

Gaede and Geryk pumps permitted reaching and holding a vacuum of less than 0.0001 mm. in the apparatus. The outlets F and K were so arranged that either portion of the main apparatus or both could be exhausted at will. For producing the discharge in AB, the best source of potential was found to be a large static machine, which was not of doubtful or changing polarity as would be the case with an induction coil. The voltage employed was determined by the use of an auxiliary spark gap. The discharges in the tube E and in the comparison spectrum tubes were produced by means of a small induction coil.

IV. CONSTRUCTION AND MANIPULATION.

Much difficulty was at first experienced in the construction of a thin, and yet gas-tight diaphragm at U. To begin with, aluminium foil was used. It was found that the best imported foil was about 0.003 mm. in thickness and was not at all free from holes. Indeed it was impossible to find an area of more than 3 or 4 square mm. which did not have a hole in it. The thinnest aluminium foil which could be obtained in New York City was 0.020 mm. thick, and quite useless because of the immense number of holes in it.

But by using the best white Indian mica and carefully splitting it up with a wedge pointed laparotomy needle, it was possible to obtain sheets of mica of the required dimensions between 0.002 and 0.006 mm. thick, and free from all visible imperfections. These sheets of mica were sealed in place with De Khotinsky cement which was sprinkled carefully over the sealing metal surfaces in the form of powder and then melted into a smooth film, thus insuring gas-tight contact. Both the front and rear surfaces, U and V, were thus treated and firmly screwed together while hot with the diaphragm between them.

Careful tests repeated many times established the fact that when the pressure on one side of the diaphragm was 0.0001 mm., the pressure on the other side might be 2,000 times as much without any perceptible leakage occurring in intervals of an hour or more.

In operation, the tube AB was exhausted to a pressure of a few hundredths of a mm. or less and the portion CKD to below 0.0001 mm. The discharge in AB from the static machine was then started. In order to eliminate so far as possible the foreign gases occluded in the electrodes or glass of the main tube, the discharge was run in one direction for some hours and then in the reversed direction for some hours with the pumps working all the time. The capillary discharge tube E received similar treatment. At the same time the air-tightness of the diaphragm was tested.

A pink fluorescence at certain spots of the tube, accompanied by considerable heating, was at times observed. This phenomenon was first described by J. E. Lilienfeld¹⁴ and explained by Gehrcke and Reichenheim¹⁵, who showed that it was due to cathode rays coming from secondary cathodes on the walls of the tube.

The potential in the main tube was adjusted by altering the pressure therein. On running a discharge through E, the spectrum of the gas which had accumulated in CKD could be examined. In order to get a bright spectrum with only small quantities of gas present, all the gas in D was compressed to several thousand times its original pressure by running mercury from H through I and D to I and then shutting the cock I. A brilliant discharge was then obtained in E.

For a time the mercury lines showed uniformly in the apparatus, and it was thought necessary to freeze out the mercury with liquid air. G was added for this purpose. It proved, however, that the improved construction which was then adopted with a stop-cock at the top of the compression reservoir prevented the mercury from volatilising, because the cock could be kept shut during the discharge. The capillary electrodes were never permitted to come into contact with the liquid mercury which clings to them tenaciously.

A preliminary test then showed that after putting fresh air into the apparatus, running the main tube for 15 minutes with the capillary portion isolated, and compressing the gas from the space D into E, only a weak air spectrum could be detected in the capillary tube E when a discharge was passed through it.

That the spectrum of the gas which reaches CKD may be expected to be visible is shown by the following roughly approximate calculation. Let it be assumed that the current through the main discharge tube is I, and that the fraction I/R of the current carrying positive ions of the kind finally identified in the capillary compression chamber pass through the diaphragm. These may not be charged atoms of the gas with which the main tube has been filled, but may be previously occluded hydrogen atoms which have been shot through the diaphragm, and in this case the fraction I/R may become quite small. On the other hand, if the charged atoms of the gas with which the tube is filled can pass through the diaphragm, I/R will be much larger. Assume also that a spectrum can be observed in the capillary tube when the pressure is I/P atmospheres.

Let that portion of the gas in CKD which is trapped in the compression chamber be I/n of the whole, and let the volume of that chamber be V cc. When the gas contained therein is compressed

into the capillary, let the compression ratio be c:1. The charge on an ion is e.

The current through the diaphragm is I/2R. Thus I/2R e ions pass through the diaphragm per second. The number of these which reach each cc. of the compression bulb after t seconds is I t/2 R e n V. When these are compressed into the capillary, there will be present in each cc. I t c/2 R e n V ions which have become neutralised by the addition of negative electrons, that is, molecules.

If under normal conditions of temperature, there are N molecules per cc. in a gas at atmospheric pressure, the observation of a visible spectrum requires that

$$\frac{I \ t \ c}{2 \ R \ c \ n \ V} = \frac{N}{P}, \quad \text{and therefore}$$

$$t = \frac{2 \ R \ e \ n \ V \ N}{P \ I \ c}.$$

The following are estimated and approximate values of the quantities present in the formula: $N=2.7(10)^{19}$, $R=(10)^6$ when the tube is filled with gases other than those finally detected back of the diaphragm, or $R=(10)^3$ when the tube is filled with a gas which is later found back of the diaphragm, $e=4.9 (10)^{-10}$ E. S. U., $I=1.5 (10)^6$ E. S. U., n=3, $P=2.5 (10)^5$, $c=5 (10)^3$, V=100.

Depending on the value of R which applies, t = 4,000 or 4 seconds. The values observed were one-half and ten times these calculated quantities respectively, so that this extremely rough approximation is consistent with the results obtained.

V. EXPERIMENTS IN VARIOUS GASES.

The actual course of the experiments was as follows. After taking the precautions outlined above to ensure the absence of any further large evolution of gas from the electrodes or of leakage through the diaphragm, the tube was run steadily at nearly constant voltage. The gas in the capillary tube was then spectroscopically examined after compression, and showed only a weak air spectrum due to unremoved air.

With the main tube containing air, and a voltage across it of 35,000, after 60 minutes running only the air spectrum of less than its original brightness showed in the capillary. After 90 minutes, however, a weak hydrogen spectrum showed which steadily became more brilliant till a very clear and complete hydrogen spectrum showed after 150 minutes. This spectrum was compared line for line with various standard spectrum tubes which could be compared with each other, and the identification of the hydrogen spectrum was complete. On reducing the voltage across the main tube to 25,000 by increasing the pressure, 120 minutes were required to show a weak hydrogen spectrum; and when the voltage was reduced to 8,000 with the corresponding rise in pressure, no hydrogen spectrum could be seen even after 300 minutes.

Carbon dioxid, carefully freed from water vapor, was then substituted for air in the apparatus. With a voltage of 28,000 the hydrogen spectrum showed after 30 minutes, and as before the spectrum became stronger with time. When the voltage was reduced to 22,000, 60 minutes were required for a visible spectrum. And with a voltage of 6,000 only an extremely doubtful trace of a hydrogen spectrum was observed after 360 minutes.

When argon was placed in the apparatus, it was hard to get a brilliant discharge through the main tube at the lower pressures, and the fluorescence was comparatively dim. With a voltage of 40,000 after 120 minutes a faint hydrogen spectrum was found, which spectrum became more brilliant and complete after continued running. When the voltage was 34,000, 180 minutes were needed for the development of a faint hydrogen spectrum. A prolonged test, wherein the tube was run at 8,000 volts for over 400 minutes showed no hydrogen spectrum.

To remove all traces of argon, which, as several investigators found, clings tenaciously to the electrodes, the tube was washed out repeatedly with air, the electrodes being approximately freed from occluded gas by constant powerful discharges through the main tube and the capillary portion.

Helium was then introduced. As before, the hydrogen spectrum was visible after 60 minutes running when the discharge voltage was 25,000, and 120 minutes sufficed when the voltage was 20,000. At 8,000 volts it was believed that the hydrogen lines could be very faintly seen after 300 minutes running, but since these lines re-

mained extremely dim even after continued running, this observation was regarded as of little weight.

There was one important respect in which helium differed from the other gases examined, namely, that while the hydrogen spectrum developed in time in the capillary, the helium spectrum did the same. Attention was first directed to this point by the brightness of the helium lines which appeared in the discharge capillary with the hydrogen lines after continued running. It was found that both hydrogen and helium passed through the diaphragm.

From the nature of the first experiments, since the apparatus was in any case filled with helium, it was doubted whether this observation was due to actual passage of the helium through the diaphragm. To test this point further, the main tube was filled with helium at appropriate pressure, and the portion CKD was washed out with air and then pumped to a low pressure. Thus there was no helium spectrum obtained from the capillary discharge tube at the beginning of the experiment. Experiment then showed that helium did accumulate in the capillary at what was estimated as more than fifty times the rate of accumulation of hydrogen. The helium passed through the diaphragm at 20,000 volts and probably also at considerably lower voltages.

This result is quite explicable, for J. J. Thomson found that in helium, the canal rays were made up of hydrogen atoms, hydrogen molecules, and helium atoms. The large preponderance of the helium atoms in the discharge tube and their consequent carriage of the greater part of the current account for the rapid rate at which the helium passed through the diaphragm.

The main tube was then filled with hydrogen, and the capillary portion with air, the tube and electrodes being first thoroughly cleaned as in the case of argon. Experiment showed that even with so low a voltage as 10,000 and 300 seconds for the discharge period, the hydrogen spectrum was visible in the capillary. At higher voltages, the time was more than proportionally diminished.

A number of tests were made to determine the effect of a mixture of hydrogen and air in the main tube. Mixtures of hydrogen and air in known proportions were therefore placed in the main tube, and air alone in the capillary portion. The influence of the hydrogen present in the main tube on the time of appearance of the hydrogen spectrum was very marked. Whereas pure air in

the main tube yielded at 25,000 volts a hydrogen spectrum in the capillary in 7,200 seconds, 0.1% of hydrogen mixed with the air reduced this time to 900 seconds, 1.0% of hydrogen to 200 seconds, 10% of hydrogen to 100 seconds, and 50% or more of hydrogen reduced the time of appearance of the hydrogen spectrum to practically the same value as for pure hydrogen, namely, 60 seconds. Similarly, at the lower voltage of 10,000 pure air showed no hydrogen spectrum in the capillary after 18,000 seconds, and 0.1% of hydrogen nothing after 9,000 seconds, yet 1.0% of hydrogen showed the hydrogen spectrum after 600 seconds, and greater percentages of hydrogen acted practically the same as pure hydrogen.

Finally a test, wherein air containing 1% of helium was used in the main tube, gave a result quite similar to that described above for hydrogen. That is, the helium spectrum appeared in 360 seconds as against 90 seconds for the case where the discharge tube was filled with pure helium. However, air to which about 3% of argon was added showed no trace of argon in the capillary tube even after 12,000 seconds, so that clearly the argon atoms do not pass through the diaphragm as do the hydrogen and helium atoms.

To ascertain whether the retrograde and cathode rays would show similar effects, the polarity of the electrodes on the main tube was reversed in several tests. No hydrogen or helium spectrum was detected at any time under these circumstances. This experiment afforded an additional proof that the hydrogen found in the capillary was actually due to the canal rays.

In the above experiments attention was fixed on the red hydrogen line (C) because of the ease with which it can be identified. Its position was found from a standard comparison spectrum tube at the time of observation and also from the previously calibrated scale of the spectrometer. Since the time of appearance of this line depended on visual acuity and sensitiveness, that is, on physiological factors, not any great accuracy can be attached to the numerical estimates of the time of first appearance of the spectrum. Experience and the maintenance of nearly constant conditions reduced the errors, it is believed, to a small value.

In every case (except for the lowest voltage used with each gas) the discharge in the main tube was continued until the entire

spectrum was so clear and unmistakable as to check perfectly with the comparison spectrum even with casual visitors observing. Traces of lines not checking with the comparison spectra were carefully searched for, but no unidentified lines were found.

VI. ELECTRIC AND MAGNETIC DEFLECTIONS.

An attempt was made to further identify the moving particles which passed through the diaphragm by obtaining their electric and magnetic spectra by the method of Thomson and Wien. In this case, all the holes but one in the front plate U were blocked, and a fine bore tube was placed back of this hole. The apparatus was so arranged that the beam of canal rays was to pass through a magnetic field of known strength and between aluminium plates maintained at a known difference of potential. They were then to strike a fine grained screen of willemite, where their point of impact was to be marked by a bright spot.

The following calculation, however, made it questionable whether the particles which passed through the diaphragm would have a high enough velocity to produce detectable fluorescent effects. Consider the hydrogen atoms which pass through the diaphragm. Imagine that these ions owe their entire velocity to the potential gradient actually existing in the main tube through which they have passed. Let m be the mass of an ion, v its velocity, V the difference of potential of the main tube electrodes, and e the charge of the ion. Then

$$I/2 m v^2 = V e$$
.

But for hydrogen V is approximately 30,000 volts, $e/m=10^4$ E. M. U.=3 (10)¹⁴ E. S. U., and therefore v=2.5 (10)⁸ cm. per second. Similarly the value for the helium atom is v=1.7 (10)⁸ cm. per second. It must be remembered that these are the velocities of the ions at the instant that they strike the diaphragm; their velocity after passing through the diaphragm is undoubtedly much lower. The α particle, which is a charged helium atom, has not been actually observed to produce ionisation (as detected through fluorescence) at lower velocities than 6 (10)⁸ cm. per second, 27% of the maximum velocity. But it is quite possible and even highly probable that it can penetrate matter at lower velocities. So that, though the atoms of hydrogen and helium pass through the diaphragm, their

passage was not regarded as proof that they might be expected to show a bright spot on the willemite screen.

Another possible factor in the production of fluorescence must also be considered, namely that the fluorescence may be dependent on the charge carried by the ion as well as on its velocity. Thus, though the velocity of the atoms which pass through the diaphragm might be above the value determined by J. Stark¹⁶ to be necessary for a positive ion to produce fluorescence, yet the neutralisation of the charge of the ion on its passage through the diaphragm might prevent the subsequent appearance of fluorescence.

A considerable number of experiments with air, hydrogen, and helium showed that no bright spot could be obtained. The pressure and voltage in the tube were varied through the widest attainable limits, and powerful oscillatory discharges were sent through the main tube as well as the unidirectional discharges. The space back of the diaphragm was pumped to the lowest vacua so that the passage of the rays would not be impeded, the eye of the observer was specially rested to secure maximum visual sensitiveness, and the hole through which the ions passed had its dimensions altered several times. Finally the original diaphragm was replaced by one of less than 0.001 mm, in thickness. In no case could any definite bright spot be detected.

VII. CONCLUSIONS.

- 1. Canal rays made up of ions of hydrogen or helium can be given sufficient velocity to cause them to pass through thin material partitions.
- 2. When the discharge tube is filled with air, carbon dioxid, or argon the only rays that pass through a thin partition are hydrogen.
- 3. When helium is used, both helium and hydrogen atoms pass through the partition, the helium in great abundance.
- 4. When hydrogen is used, only hydrogen atoms pass through the partition, and these in large quantities.
- 5. The atoms which pass through such a partition are not capable of causing fluorescence on screens.

In conclusion, I desire to express my thanks for the assistance

rendered by Professor Bergen Davis, at whose suggestion this research was undertaken, and who has frequently placed his wide knowledge of the subject and experience in experiment at my disposal.

PHŒNIX PHYSICAL LABORATORIES,
COLUMBIA UNIVERSITY, August, 1911.

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VITA.

Alfred Norton Goldsmith was born in New York City, New York, September 15th, 1887. In 1907 he was graduated from the College of the City of New York, receiving from that institution the degree of Bachelor of Sciences, cum laude. He was elected to membership in Φ B K in 1907, and also appointed to a Fellowship at the College of the City of New York, which Fellowship he held till 1910. During the years of 1907 to 1911 he was a Graduate Student under the Faculty of Pure Science of Columbia University. Tutor in Physics at the College of the City of New York, 1911. His previous publications are

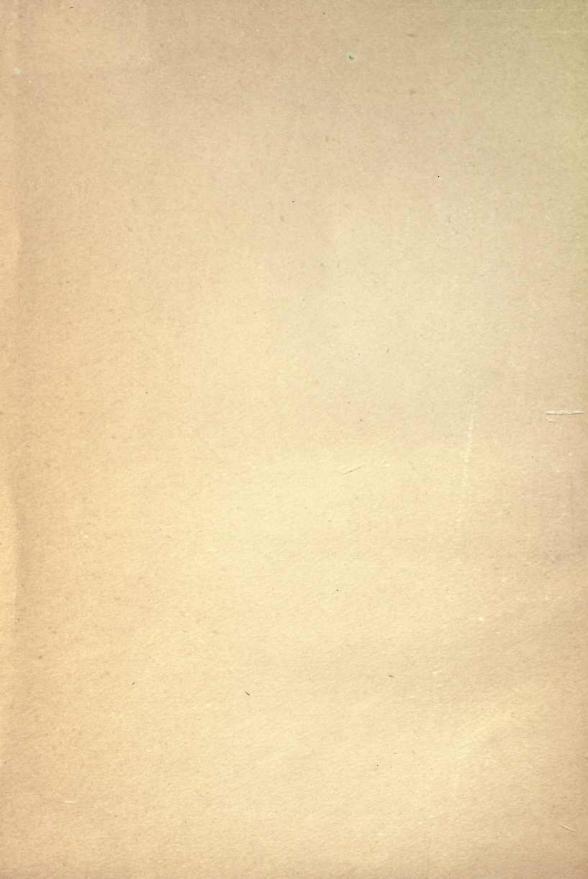
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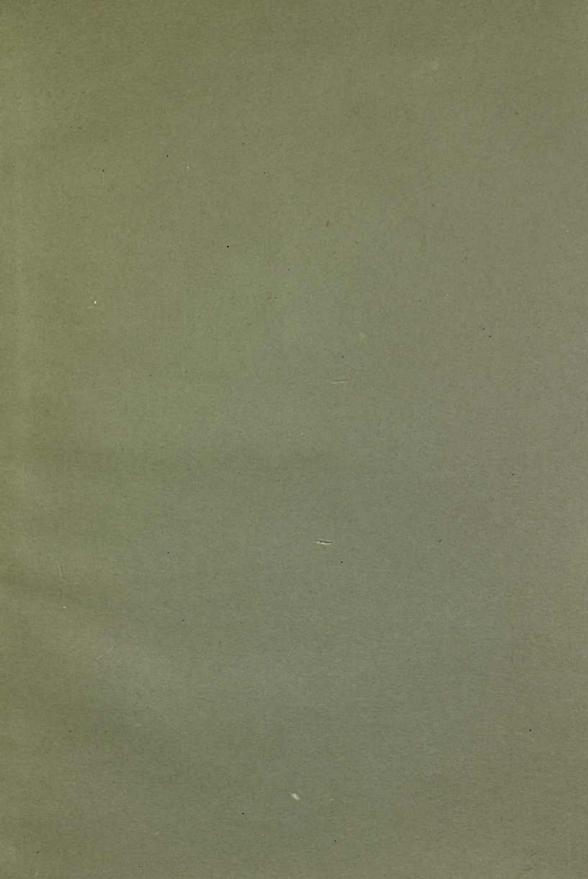
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